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# Thermal analysis of wood fuel pyrolysis process

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**Abstract.** The paper presents the results of studies of conversion process on the laboratory pyrolysis reactor and the results are compared with data, obtained in model experiments by thermogravimetric analysis (TGA). The heating rates were compared in the pyrolysis reactor and in the laboratory furnace of TGA in the pyrolysis process of wood biomass conversion. The laboratory pyrolysis reactor, as a part of the multistage gasification facility of low-grade solid fuel, was launched in several modes. Three experimental modes of the device operation with different screw speeds and fuel flow rates through the reaction shaft were tested. The temperature profile of fuel and wall along the length of the pyrolysis reactor was shown. The temperature up to 600 °C was recorded in a mode with a low fuel flow rate, and in the end of the reaction zone the fuel temperature was close to that of the wall. The kinetic coefficients and conversion rates for the wood biomass pyrolysis were calculated from the obtained equation. Therefore, the calculated data of the conversion rate and the pyrolysis parameters, based on the TGA data, can be used to further develop the pyrolysis reactor and evaluate the parameters of its operation.

## 1. Introduction

At present, the involvement of low-grade solid fuel in the energy balances of Russian regions becomes ever more significant. Technologies aimed at effective use of bioresources are actively developed and implemented abroad [1].

The increase in solid fuel conversion efficiency is possible if the conversion is divided into several stages: thermal preparation, burning of combustible gases, and gasification of solid residue [2]. The most important stage is the thermal preparation of the raw wood material – the pyrolysis process.

One of the methods of studying conversion processes is thermogravimetric analysis. The analysis of a small sample with a high-precision instrument allows studying in detail the conversion (pyrolysis) and obtaining data on the conversion rate and the evolved gas composition at different heating rates. A small sample ensures minimum costs and high efficiency (homogeneity, exact correspondence of the real conversion regimes to given conditions) as well as a large number of modes and a choice of optimal conditions for research at larger facilities.

When it studying the conversion process at large facilities, it is difficult to measure process parameters, there is a limited number of measurement points and irregularity of the process. Furthermore, additional difficulties connected with a restrictions in researched modes because it takes a long time to reach the set operation mode but the resource of equipment is limited too.



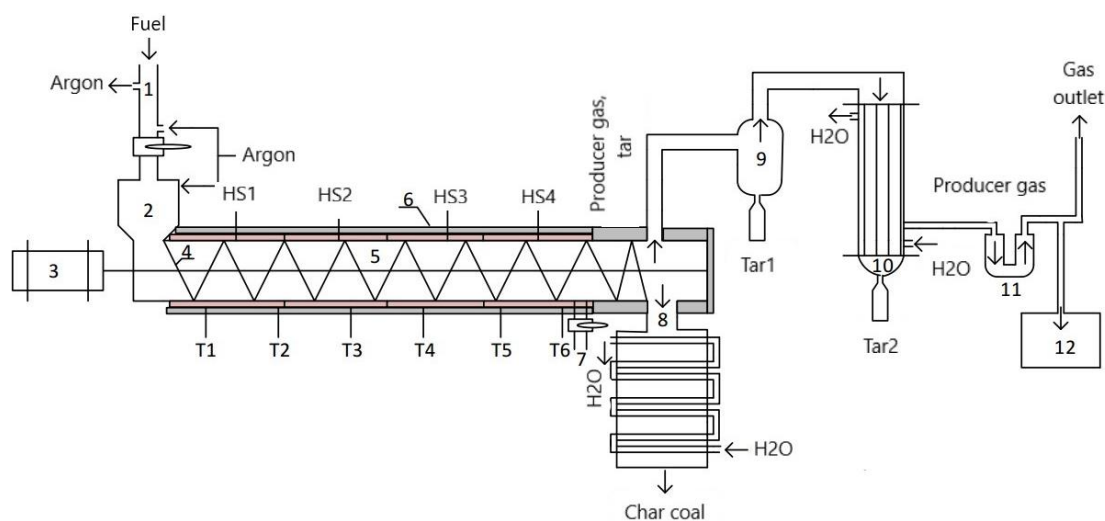
When methods are used conjoint, there is a problem of conformity of experimental data and the process conditions in the TGA and in the pyrolysis reactor. The aim of this study was to compare conversion conditions in TGA and pyrolysis reactor and to supplement the experimental results from the facility with data obtained with TGA.

## 2. The pyrolysis reactor

The pyrolysis reactor is the first stage of multistage gasification of the conversion facility, currently being developed at the Melentiev Energy Systems Institute [3]. The multistage gasifier consists of three units: pyrolysis reactor, afterburner reactor of pyrolysis gas and tar and last gasification reactor.

The screw pyrolysis reactor is the first stage of the gasifier, as the initial fuel moves along the reactor shaft, rotated at a variable speed by the drive. Fuel is heated through the outer surface. In the multistage gasifier, the pyrolysis reactor is proposed to be heated by gaseous coolants: the exhaust gases of the internal combustion engine and the generator gas blown through the pyrolysis reactor casing. A numerical simulation of the pyrolysis reactor was preliminarily carried out and the reactor temperature profile was previously estimated on the CFD model [4].

Parameters of the pyrolysis reactor: the length of the reaction zone is 1600 mm, the diameter is 145 mm, and the appearance of the pyrolysis reactor is shown in figure 1. The fuel is transported through the reactor shaft (5) by means of a screw (4) rotated by a variable speed drive (3). Heating of the fuel is carried out by four sections of the electric heater HS1-HS4, located on the outer surface of the reaction shaft, which is covered with a layer of thermal insulation (6).



**Figure 1.** Preliminary design of the laboratory pyrolysis reactor.

The small amounts of fuel are loaded into the fuel tank (1), which is purged with argon to remove air. Then the fuel enters the storage reservoir (2) through a airtight gateway. To calculate fuel consumption, the time of each fuel sample arrival into the storage reservoir is recorded.

The bulk of the reacted fuel enters the cooled ash tank (8). The charcoal sampling to determine its technical characteristics is realized through the sampler (7). The pyrolysis gas and tar enters the cyclone (9), in which solid particles and high-boiling tar (tar 1) are separated. The pyrolysis gas is cooled in a heat exchanger (10), in which the low-boiling tar (tar 2) is separated, and then, gas passes through a filter (11). The yield of liquid pyrolysis products of wood fuels is estimated by the weight of the tar samples taken from the cyclone (9) and the heat exchanger (10).

The temperature of the pyrolysis reactor wall was measured by thermocouples T1-T6, and the temperature of the fuel bed was measured by thermocouples that were immersed in the bed during the experiment. The direct measurement of the yield of gaseous pyrolysis products was hindered by tar products precipitated on the internal surfaces of the measuring equipment. To estimate the yield of

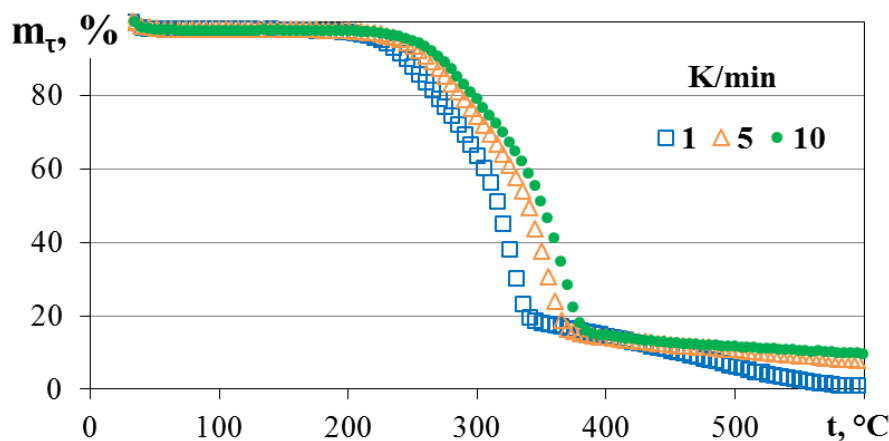
pyrolysis gas, a balance was used for the inert gas-marker-argon, a certain amount of which was continuously supplied to the unit. The composition of pyrolysis gas was determined by gas chromatography. The sum of absolute errors in measuring the concentrations of gas components did not exceed 1 %.

### 3. The wood sample conversion by TGA

The TGA method is often used for a detailed study of mass transfer processes under external influence of a gaseous medium and temperature change. With high accuracy the change sample mass, the thermal effects of the process and the composition of the outgoing products in the gas phase are fixed. Thus, using the thermal analysis instrument, it is possible to experimentally simulate conversion processes, in particular pyrolysis [5, 6], occurring in pilot and industrial facilities.

#### 3.1. TGA research of wood fuel pyrolysis

The wood samples were placed in thermal analysis unit – NETZSCH STA 449F3 with a standard TGA-DSC holder and heated in an inert atmosphere of argon at a rate of 1, 5, 10 K/min from 35 to 600 °C. The dependence of the mass loss rate on the temperature of the process is presented in figure 2.



**Figure 2.** Sample mass loss rate with increasing process temperature.

The sample is aspen chips biomass ( $1 \times 1$  cm); it is raw wood material with the following characteristics: density of  $220 \text{ kg/m}^3$ , ash content of 0.1 %, and volatile matter of 81.7 %. It should be noted that the active phase of the devolatilization is completed at a temperature of 350-380 °C, regardless of the heating rate.

#### 3.2. The calculation procedure

The relationships between the rate of conversion and time, temperature and degree of sample conversion were calculated during the experiment. Kinetic parameters were obtained using a verified calculation method. For the analysis of current values, it is expedient to use the conversion rate  $R_\tau$ , 1/s:

$$R_\tau = \frac{1}{m_\tau} \frac{dm_\tau}{d\tau} = \frac{1}{1-X} \frac{dX}{d\tau} \quad (1)$$

where  $m_\tau$  is the mass of carbon in the sample at the present time, mg; and  $dm/d\tau$  is the rate of organic mass loss in time, mg/s.

The conversion degree of wood organic mass is defined as the ratio of the weight loss at the current time to the total loss of sample mass.

The Arrhenius equation can be used to express the constants of the chemical reaction rate:

$$\frac{dX}{d\tau} = k(T)f(X)p_g^n \quad (2)$$

Nonisothermal curves are formed under the influence of two factors: a stepwise supply of an oxidizer and a temperature that increases linearly over time, transforming into an exponentially increasing reaction rate constant with the limiting action of the reactive substance decreasing with time.

The apparent constant of the chemical reaction rate of a fuel is determined as follows:

$$k(T) = k_0 \cdot \exp(-E_a / RT), \quad (3)$$

where  $k_0$  is the pre-exponential factor (frequency factor), 1/s;  $E_a$  is the activation energy, kJ/mol;  $R$  is the universal gas constant, kJ/mol·K; and  $T$  is the process temperature, K.

The main objective of the analysis of the conversion process is to choose a model for the conversion [7, 8] of fuel particle  $f(X)$ , which most reliably describes the interaction between reactant gas and solid fuels. The volumetric reaction model assumes that the reaction proceeds throughout the entire volume of a particle, with an initial diameter maintained, and density and porosity of the particle changing in the course of conversion. Assuming that the function  $f(X) = (1-X)$ , and taking into account the constant value of the reactant gas concentration (i.e. using equations (3) and (4)), the rate of sample conversion may be written as follows:

$$\frac{dX}{d\tau} = k_0 \cdot \exp(-E_a / RT)(1-X), \quad (4)$$

The yield of volatiles is described by a one-stage reaction of the  $n$ -th order. This approach was implemented in many studies on kinetics of volatiles [9].

Then from (4) and (1), the following equation is derived:

$$R_t = k_0 \cdot \exp(-E_a / RT), \quad (5)$$

Thus, according to the Arrhenius equation, the activation energy and the pre-exponential factor were determined for all the fuel samples curves, for which the values of the reaction rate constants for different wood samples were calculated and the kinetic data were identified.

## 4. Result and discussion

### 4.1. Experimental study of the wood fuel pyrolysis

According to experiments at the laboratory pyrolysis reactor, the yield of the solid phase (coke) was 18.5 %, which corresponded to the thermal analysis data of the pyrolysis process.

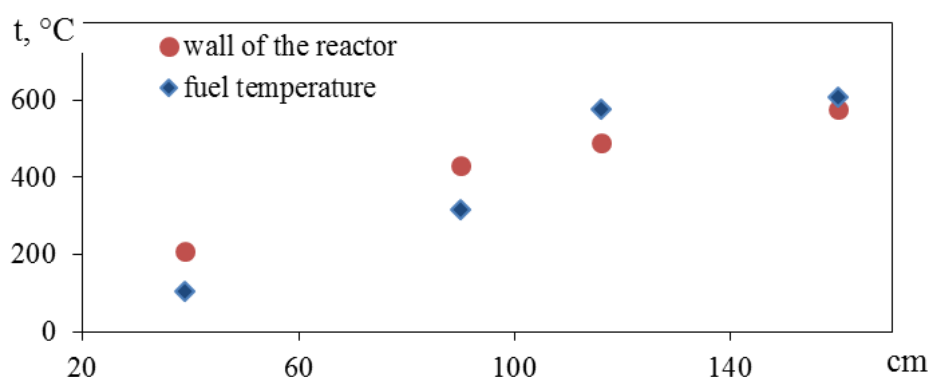
On the screw pyrolysis reactor, an experimental launch was started on wood pellets. At experimental launch, three modes of the device operation with different screw speeds and the fuel flow rate through the reaction shaft (table 1) were tested.

**Table 1.** Experimental data of pyrolysis modes.

Index	Measurement unit	Mode 1	Mode 2	Mode 3
Linear velocity of fuel	mm/s	0.19	0.36	0.62
Fuel consumption	kg/h	4.40	8.63	15.68
Power by fuel	kW	20.5	40.3	73.2
The residence time of fuel in the reactor	min	144	73	43

An increase in the fuel supply rate caused changes in the temperature profile of the reactor wall, the temperature was naturally reduced and heat was transferred from the reactor with the conversion products. The highest temperature of the fuel (up to 600 °C) was recorded in a mode with low fuel velocity (mode 1), and at the end of the reaction zone the fuel was heated close to the reactor wall temperature. In mode 2, the final fuel temperature was 400 °C that was about 200 °C below the wall temperature. In mode 3, with the highest rate of fuel transfer from the tested modes, the temperature difference between the wall and the fuel was even higher and reached 270 °C.

The figure 3 shows that the temperature profile in mode 1 along the length of the reactor matches with the wall temperature closer to the exit from the pyrolysis reactor.



**Figure 3.** The temperature profile along the reactor length in mode 1.

The efficiency of fuel heating in the modes was significantly different during the transition from one heating section to another. The greatest efficiency was specific for a segment from 50 to 120 cm along the length of the reactor.

In the first segment length of 50 cm the fuel was heated the least efficiently, heating reached only 70-80 °C in mode 1. Increase productivity of the pyrolysis reactor was possible with an increase in the temperature of the reactor walls (with using a high-temperature profile). In this case, it will be possible to raise the pyrolysis reactor power by increasing the fuel residence time in the reactor areas heated to 500-600 °C.

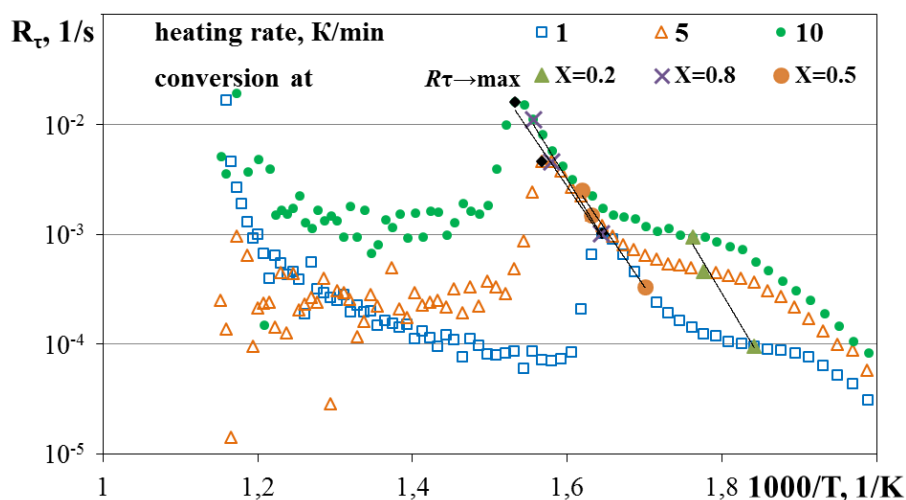
#### 4.2. The kinetic parameters of wood samples

The relationship between the conversion rate and reciprocal temperature for different heating rates is shown in figure 4. The line for the kinetic parameters calculation was selected at different points along the length of the reactor. The conversion process in the case of the initial wood consists of a variety of reactions taking place during the yield and transformation of volatile substances, which greatly complicates the calculation of kinetics.

Figure 4 demonstrates the lines connecting the points at different conversion degrees  $X = 0.2, 0.5, 0.8$  and at the maximum conversion rate  $R_{\tau \rightarrow \max}$ . Thus, according to the Arrhenius equation, the activation energy and the pre-exponential factor were determined for fuel samples.

The kinetic coefficients for the conversion of wood biomass were calculated from the obtained equation (6) at the maximum conversion rate. The calculated pre-exponential factor  $k_0$  is  $8.2 \cdot 10^{-11}$  1/s, and the activation energy  $E_a$  is 106.8 kJ/mol.

When comparing the data obtained in the TGA and data of the laboratory pyrolysis reactor, it may be noted that the average integral heating rate of fuel during the movement of the screw in the mode 1 is about 5 K/min, which corresponds to one of the regimes in TGA studies.



**Figure 4.** Rate of conversion against reciprocal temperature at varying heating rate.

The maximum rate of fuel heating in the central part of the pyrolysis reactor is 10 K/min. Therefore, the data on the conversion rate and the calculated parameters of the pyrolysis process, based on the TGA data, can be used to further develop the pyrolysis reactor and evaluate the parameters of its operation.

## 5. Conclusions

From the comparison of experimental data of the pyrolysis stage with results of TGA studies it can be concluded that the most suitable for the realization of the multistage process is the mode with the least fuel flow rate along the reactor shaft (mode 1). Such regime provides low rates of heating of the supplied fuel, thereby achieving a low yield of residual volatile in charcoal and a high calorific value of the pyrolysis gas, which generally improves the efficiency of the wood fuel preparation process.

The resulting kinetic coefficients will be used in future to simulate the pyrolysis of wood fuels using the developed kinetic-thermodynamic and CFD models. The conversion parameters data, obtained by the TGA, can be used to further estimation of the pyrolysis reactor operation parameters and its modification.

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